(12) **EUROPEAN PATENT APPLICATION**

(71) Applicant: MOBIL OIL CORPORATION
150 East 42nd Street
New York New York 10017(US)

(72) Inventor: La Pierre, Rene Bernard
43 Arrowhead Court
Medford New Jersey 08055(US)

(72) Inventor: Partridge, Randall David
58 Jacobs Creek Road
West Trenton New Jersey 08628(US)

(72) Inventor: Wong, Stephen Sul Fal
3 Carrol Joy Road
Medford New Jersey 08055(US)

(74) Representative: Cooper, John Anthony et al,
Mobil Court 3 Clements Inn
London WC2A 2EB(GB)

(54) Hydrocracking process using zeolite beta.

(57) A hydrocracking process for gas oils and other high boiling petroleum fractions using an initial hydrotreating step to remove heteroatom impurities, is carried out at hydrogen partial pressures below 10,000 kPa using a hydrocracking catalyst based on zeolite beta. The process produces highly paraffinic, low pour point distillate products useful as jet fuels and diesel fuels. The process is capable of operating at high conversions with low catalyst aging rates and low specific hydrogen consumption.

HYDROCRACKING PROCESS USING ZEOLITE BETA

This invention relates to a process for catalytically hydrocracking hydrocarbon chargestocks to produce low pour point distillate products of reduced viscosity.

Hydrocracking is a process which has achieved widespread use in petroleum refining for converting various petroleum fractions into lighter and more valuable products, especially gasoline and distillates such as jet fuels, diesel oils and heating oils. Hydrocracking is generally carried out in conjunction with an initial hydrotreating step in which the heteroatom-containing impurities in the feed are hydrogenated without a substantial bulk conversion of the feed. During this step, the heteroatoms, principally nitrogen and sulfur, are converted into ammonia and hydrogen sulfide and these gases may be removed prior to the subsequent hydrocracking step although the two stages may be combined in cascade without interstage separation, for example, as in the Unicracking-JHC Process and as described in U.S. Patent 4,435,275. However, the presence of large quantities of ammonia in the hydrotreating effluent may result in a significant suppression of cracking in the subsequent hydrocracking step although this may be compensated by an increase in severity.

In the subsequent hydrocracking step, the hydrotreated feedstock is contacted with a catalyst which has both an acidic function and a hydrogenation function. In the first step of the reaction, the polycyclic aromatics in the feedstock are hydrogenated, after which cracking takes place together with further hydrogenation. Depending upon the severity of the reaction conditions, the polycyclic aromatic in the feedstock will be hydrocracked down to paraffinic materials or, under less severe conditions, to monocyclic aromatics as well as paraffins.

The acidic function in the catalyst is provided by a carrier such as alumina, silica-alumina or a crystalline zeolite such as faujasite, zeolite X, zeolite Y or mordenite. Large pore zeolites have proved to be highly useful catalysts for this purpose because they possess a high degree of intrinsic cracking activity and, for this reason, are capable of producing a good yield of gasoline. They also possess a better resistance to nitrogen and sulfur compounds than the amorphous materials such as alumina and silica-alumina.

The hydrogenation function is provided by a metal or combination of metals. Noble metals of Group VIIIA of the Periodic Table (the Periodic Table being that approved by IUPAC), especially platinum or palladium may be used, as may base metals of Groups IVA, VIA and VIIIA, especially chromium, molybdenum, tungsten, cobalt and nickel. Combinations of metals such as nickel-molybdenum, cobalt-molybdenum, cobalt-nickel, nickel-tungsten, cobalt-nickel-molybdenum and nickel-tungsten-titanium have been shown to be very effective and useful.

In EP-A-94827, there is described a hydrocracking process which, besides achieving a bulk conversion of the feedstock, also dewaxes it. The zeolite catalyst component used in that process, zeolite beta, has a number of highly useful and characteristic properties. First, it shows a significant distillate selectivity; that is, it tends to produce hydrocracked products boiling in the distillate range (about 165°-345°C) as opposed to conventional hydrocracking catalysts which are naphtha-directing and which tend to produce a gasoline boiling range (about C_5 to 165°C) product. Although this behavior is shared by other highly siliceous zeolites such as high-silica Y and high silica ZSM-20, zeolite beta also has the unique ability to hydroisomerize and hydrocrack the paraffinic components of the feed. This is in marked contrast to the behavior of other zeolites such as zeolite Y: if a waxy feedstock is hydrocracked with a conventional large pore catalyst such as zeolite Y, the viscosity of the oil is reduced by cracking most of the 343°C+ material into lower boiling products. The remainder of the 345°C+ material that is not converted, however, contains the

majority of the paraffinic components in the feedstock because with
these conventional catalysts the aromatics are converted preferen-
tially as compared to the paraffins. The unconverted 345°C+
material therefore retains a high pour point so that the final,
hydrocracked product containing the unconverted paraffins will also
have a relatively high pour point. Thus, although the viscosity is
reduced, the pour point might still be unacceptable. Even if the
conditions are adjusted to give complete or nearly complete conver-
sion, the higher molecular weight hydrocarbons which are present in
the product will contain a substantial proportion of straight chain
components (n-paraffins). If these are of sufficiently high
molecular weight themselves (as they often are) they will constitute
a waxy component in the product. The final product may therefore be
proportionately more waxy than the feedstock (because the non-
paraffinic components have been selectively removed by cracking)
and, consequently, may have a pour point which is equally unsatis-
factory or even more so. Attempts to reduce the molecular weight of
these straight chain paraffinic products will only serve to produce
very light fractions, for example propane, butanes and light naphtha,
so decreasing the desired liquid yield.

Zeolite beta, by contrast, removes the paraffinic components
so that a dewaxing effect is achieved simultaneously with the bulk
conversion. So, if a gas oil containing paraffins, naphthenes and
aromatics is treated under hydrocracking conditions with a zeolite
beta catalyst, all three types of hydrocarbon will be converted
whereas other zeolites would selectively hydrocrack the naphthenes
and aromatics and concentrate the paraffins.

As mentioned in EP-A-94827, a preliminary hydrotreating
step is desirable in order to remove nitrogen and sulfur and to
saturate aromatics to naphthenes without substantial bulk
conversion. The zeolite beta-catalyzed hydrocracking process is
therefore adaptable to otherwise conventional hydrocracking
operations.

It has now been found that zeolite beta hydrocracking
catalysts offer a number of advantages in hydrocracking processes

carried out at unconventionally low pressures, typically below 10,000 kPa hydrogen partial pressure. In particular, compared to a similar process using a conventional catalyst system, product quality is improved while hydrogen consumption is decreased. Specific product characteristics in which improvements may be noted include low sulfur content, Smoke Point (which is higher, that is to say better) and Diesel Index (which is higher). The products of the process are especially useful as diesel and jet fuels because of their highly paraffinic compositions coupled witn their low pour points; however, they may also be used as highly satisfactory heating oils and kerosenes because of their low pour point and sulfur content. The catalyst is, moreover, capable of maintaining hydrocracking activity over long cycles, typically about one year or longer. The zeolite beta catalyst is, in particular, noted for its ability to maintain its activity for extended periods of time even when operating at relatively high conversions under low pressures. Conventional catalysts tend, by contrast, to undergo rapid aging when operated at high conversions under low pressures, typically below 10,000 kPa.

According to the invention, there is provided a hydrocracking process for making a highly paraffinic, low pour point distillate product from a heavy hydrocarbon oil feed boiling substantially above 345°C, which comprises:

(i)   passing the heavy oil feed over a hydrotreating catalyst in the presence of hydrogen at elevated temperature and at a hydrogen partial pressure of not more than 10,000 kPa to hydrotreat the oil;

(ii) passing the hydrotreated oil from step (i) over a hydrocracking catalyst comprising zeolite beta and a hydrogenation-dehydrogenation component in the presence of hydrogen at elevated temperature and at a hydrogen partial pressure of not more than 10,000 kPa to hydrocrack the oil at a bulk conversion of at least 40 weight percent and;

(iii)   recovering from the hydrocracked product from step (ii) a fraction boiling below 345°C.

The process is operated with an initial hydrotreating step and this is followed by the hydrocracking step either with or without interstage separation. Both steps are carried out at the low pressures which characterize the process.

The feedstock for the process is a heavy oil fraction having an initial boiling point of at least 200°C and normally of at least 345°C or higher. Suitable feedstocks of this type include gas oils such as vacuum gas oil, coker gas oil, visbreaker oil, deasphalted oil and catalytic cracker cycle oil. Normally, the feedstock will have an extended boiling range, for example 345 to 590°C but may be of more limited ranges with certain feedstocks. For reasons which are explained below, the nitrogen content is not critical; generally it will be in the range 200 to 1000 ppmw. Likewise, the sulfur content is not critical and typically may range as high as 5 percent by weight. Sulfur contents of 2.0 to 3.0 percent by weight are common.

These heavy oil feeds will comprise high molecular weight long chain paraffins and high molecular weight aromatics with a large proportion of fused ring aromatics. During the processing, the fused ring aromatics and naphthenes are cracked by the acidic catalyst and the paraffinic cracking products, together with paraffinic components of the initial feedstock undergo isomerization to iso-paraffins with some cracking to lower molecular weight materials. Hydrogenation of unsaturated side chains on the monocyclic cracking residues of the original polycyclics is catalyzed by the hydrogenation-dehydrogenation component of the hydrocracking catalyst to form substituted monocyclic aromatics which are highly desirable end products. The heavy hydrocarbon oil feedstock will normally contain a substantial amount boiling above 230°C and will normally have an initial boiling point of at least about 290°C, more usually about 345°C. Typical boiling ranges will be about 345 to 565°C or about 345 to 510°C but oils with a narrower boiling range may, of course, be processed, for example those with a boiling range of about 345 to 455°C. Heavy gas oils are often of this kind as are cycle oils and other non-residual materials. It is

possible to co-process materials boiling below 260°C but the degree of conversion will be lower for such components. Feedstocks containing lighter ends of this kind will normally have an initial boiling point above 150°C.

The process is of particular utility with highly paraffinic feeds because, with feeds of this kind, the greatest improvement in pour point may be obtained. However, most feeds will contain a certain content of polycyclic aromatics; it is a notable feature of zeolite beta that it retains its ability to remove the waxy components of the feed even in the presence of substantial amounts of aromatics, for example 10 percent or more aromatics. However, the aromatic content of the feed will normally not exceed 50 percent by weight of the feedstock. Typically the aromatic content will be 20-50, more usually about 30, weight percent of the feed.

The feedstock may contain relatively large proportions of waxy hydrocarbons in the 345°C+ fraction; these waxy hydrocarbons may be characterized chemically as straight chain and slightly branched chain paraffins, that is n-paraffins and iso-paraffins having short chain branches. The higher molecular weight paraffins will generally be slightly branched chain materials as opposed to being wholly straight chain but because the branchings are relatively short, the linear chain characteristics will predominate, so that the material will be of a waxy nature, contributing to a high pour point.

In the process, the feedstock is heated to an elevated temperature and is then passed over the hydrotreating and hydrocracking catalysts in the presence of hydrogen. Because the thermodynamics of hydrocracking become unfavorable at temperatures above about 450°C, temperatures above this value will not normally be used. In addition, because the hydrotreating and hydrocracking reactions are net exothermic, the feedstock need not be heated to the temperature desired in the catalyst bed which is normally in the range 360 to 440°C. At the beginning of the process cycle, the temperature employed will be at the lower end of this range but as the catalyst ages, the temperature may be increased in order to maintain the desired degree of activity.

The heavy oil feedstock is passed over the catalysts in the presence of hydrogen. The space velocity of the oil is usually in the range 0.1 to 10 LHSV, preferably 0.2 to 2.0 LHSV and the hydrogen circulation rate from 250 to 1000 $n.l.l^{-1}$ (liters of hydrogen - measured at standard temperature and pressure - per liter of oil), and more usually from 300 to 800 $n.l.l^{-1}$. Hydrogen partial pressure is usually at least 75 percent of the total system pressure with reactor inlet pressures normally being in the range of 3000 to 10000 kPa, more commonly from 5000 to 7000 kPa. When operating at low conversions, for example, less than 50 volume percent conversion to 345°C- products, the pressure may be considerably lower than normal, conventional practices. It has been found tnat pressures of 5000 to 7000 kPa are satisfactory, as compared to the pressures of at least 10,500 kPa normally used in commercial hydrocracking processes. However, if desired, low conversion may be obtained by suitable selection of other reaction parameters, for example temperature, space velocity, choice of catalyst, even lower pressures may be used. Low pressures are desirable from the point of view of equipment design since less massive and consequently cheaper equipment will be adequate. Similarly, lower pressures usually influence less aromatic saturation and thereby permit economy in the total amount of hydrogen consumed in the process. However, certain catalysts may not be sufficiently active at very low pressures, for example 3000 kPa and higher pressures may then be necessary at the space velocities desired in order to maintain a satisfactory throughput.

In the first stage of tne process, the feed is passed over a hydrotreating catalyst to convert nitrogen and sulfur containing compounds into gaseous ammonia and hydrogen sulfide. At this stage, hydrocracking is minimized but partial hydrogenation of polycyclic aromatics proceeds, together with a limited degree of conversion to lower boiling (345°C-) products. The catalyst used in this stage may be a conventional denitrogenation (denitrification) catalyst. Catalysts of this type are relatively immune to poisoning by the nitrogenous and sulfurous impurities in the feedstock and, generally

comprise a non-noble metal component supported on an amorphous, porous carrier such as silica, alumina, silica-alumina or silica-magnesia. Because extensive cracking is not desired in this stage of the process, the acidic functionality of the carrier may be relatively low compared to that of the subsequent hydrocracking catalyst. The metal component may be a single metal from Groups VIA and VIIIA of the Periodic Table such as nickel, cobalt, chromium, vanadium, molybdenum, tungsten, or a combination of metals such as nickel-molybdenum, cobalt-nickel-molybdenum, cobalt-molybdenum, nickel-tungsten or nickel-tungsten-titanium. Generally, the metal component will be selected for good hydrogen transfer activity; the catalyst as a whole will have good hydrogen transfer and minimal cracking characteristics. The catalyst should be pre-sulfided in the normal way in order to convert the metal component (usually impregnated into the carrier and converted to oxide) into the corresponding sulfide.

In the hydrotreating (denitrogenation) stage, the nitrogen and sulfur impurities are converted into ammonia and hydrogen sulfide. At the same time, the polycyclic aromatics are partially hydrogenated to form substituted aromatics which are more readily cracked in the second stage to form alkyl aromatics. Because the process may be operated with only a limited degree of overall conversion, the effluent from the first stage may be passed directly to the second or hydrocracking stage without the conventional interstage separation of ammonia or hydrogen sulfide, although hydrogen quenching may be carried out in order to control the effluent temperature and to control the catalyst temperature in the second stage. However, interstage separation of ammonia and hydrogen sulfide and light fractions may be carried out, especially with the noble metal hydrocracking catalysts which are more sensitive to the impurities.

The effluent from the denitrogenation/desulfurization stage is passed to the hydrocracking step to crack partially hydrogenated aromatics and carry out the other characteristic reactions which take place over the hydrocracking catalyst.

The hydrocracking catalyst comprises zeolite beta at least partly in the hydrogen form as an acidic component, together with a hydrogenation-dehydrogenation component. The hydrogenation-dehydrogenation component is provided by a metal or combination of metals. Noble metals of Group VIIIA, especially platinum, or base metals of Groups IVA, VIA and VIIIA, especially chromium, molybdenum, tungsten, cobalt and nickel, may be used. Base metal combinations such as nickel-molybdenum, cobalt-nickel, nickel-tungsten, cobalt-nickel-molybdenum and nickel-tungsten-titanium are useful, although for certain applications platinum is preferred.

The content of the metal component will vary according to its catalytic activity. Thus, the highly active noble metals may be used in smaller amounts than the less active base metals. For example, about 1 weight percent or less platinum will be effective and in a preferred base metal combination, about 7 weight percent nickel and about 2.1 to about 21 weight percent tungsten, expressed as metal. The hydrogenation component can be exchanged onto the zeolite, impregnated into it or physically admixed with it. If the metal is to be impregnated into or exchanged onto the zeolite, it may be done, for example, by treating the zeolite with a platinum metal-containing ion. Suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum ammine complex. The metal compounds may be either compounds in which the metal is present in the cation of the compound and compounds in which it is present in the anion of the compound. Both types of compounds can be used. Platinum compounds in which the metal is in the form of a cation or cationic complex, for example $Pt(NH_3)_4Cl_2$ are particularly useful, as are anionic complexes such as the vanadate and metatungstate ions. Cationic forms of other metals are also very useful since they may be exchanged onto the zeolite or impregnated into it.

The acidic component of the hydrocracking catalyst is zeolite beta. Zeolite beta is a crystalline zeolite having a pore size greater than 5 Angstrom units (5×10^{-10}m). Its composition and X-ray structure are described in U.S. Patents 3,308,069 and Re

28,341, to which reference may be made for a description of this zeolite, its preparation and properties. Hydrocracking catalysts based on zeolite beta are described in EP-A-94827, to which reference may be made for a description of them.

When it is used in the catalysts for the process of the invention, the zeolite is at least partly in the hydrogen form in order to provide the desired acidic functionality for the cracking reactions which are to take place. It is normally preferred to use the zeolite in a form which has sufficient acidic functionality to give it an alpha value of 1 or more. The alpha value, a measure of zeolite acidic functionality, is described, together with details of its measurement in U.S. Patent 4,016,218 and in J. Catalysis, Vol. VI, pages 278-287 (1966) and reference may be made to these for such details. The acidic functionality may be controlled by base exchange of the zeolite, especially with alkali metal cations such as sodium, by steaming or by control of the silica:alumina ratio of the zeolite.

It has been found that steamed zeolite beta catalysts having an alpha value of from 100 to 200, preferably about 150, are preferred for the process, as compared to unsteamed catalysts having alpha equal to about 600 to 800, particularly with base metal hydrogenation-dehydrogenation components, especially nickel-tungsten, the steamed catalysts having been found to be more stable for conversion.

Because the hydrogenation functionality may also be varied by choice of metal and its relative quantity, the balance between the hydrogenation and cracking functions may be adjusted as circumstances require. The ammonia produced in the first stage will, to some degree, tend to reduce the acidic functionality of the hydrocracking catalyst but in the present process only a limited degree of conversion is desired and so the reduced cracking consequent upon the diminution of acidic functionality is not only acceptable but also useful.

The preferred forms of zeolite beta for use in the present process are the high silica forms, having silica:alumina ratios of at least 30:1. It has been found, in fact, that zeolite beta may be

prepared with silica:alumina ratios above the 200:1 maximum specified in U.S. Patents 3,308,069 and Re. 28,341. Ratios of at least 50:1 and preferably at least 100:1 or even higher, for example 250:1, 500:1 may be used.

The silica:alumina ratios referred to are the structural or framework ratios, related to the ratio of the SiO_4 to the AlO_4 tetrahedra which together constitute the structure of which the zeolite is composed. This may vary from the silica:alumina ratio determined by various physical and chemical methods. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite, thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by the thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain treatments such as the dealuminization method described below which result in the presence of ionic aluminum free of the zeolite structure, are employed. Due care should therefore be taken to ensure that the framework silica:alumina ratio is correctly determined.

The preparation of the highly siliceous forms of zeolite beta is described in U.S. Patent 4,419,220, to which reference may be made for a description of these forms and their preparation.

Prior to use the zeolite should be dehydrated at least partially. This can be done by heating to a temperature in the range of 200 to 600°C in air or an inert atmosphere such as nitrogen for 1 to 48 hours. Dehydration can also be performed at lower temperatures merely by using a vacuum, but a longer time is required to obtain a sufficient amount of dehydration.

It may be desirable to incorporate the catalyst in another material resistant to the temperature and other conditions employed in the process. Such matrix materials include synthetic and naturally occurring substances such as inorganic materials, for

example clay, silica and metal oxides, as described in U.S. Patent 4,419,220. Matrix materials may themselves possess catalytic properties, generally of an acidic nature.

The catalyst may be treated by conventional pre-sulfiding treatments, for example by heating in the presence of hydrogen sulfide, to convert oxide forms of the metals such as CoO and NiO into their corresponding sulfides.

The relative proportions of the hydrocracking and the hydrotreating catalysts may be varied according to the feedstock in order to convert the nitrogen in the feedstock into ammonia before the charge passes to the hydrocracking step; the object is to reduce the nitrogen level of the charge to a point where the desired degree of conversion by the hydrocracking catalyst is attained with the optimum combination of space velocity and reaction temperature. The greater the amount of nitrogen in the feed, the greater then will be the proportion of hydrotreating (denitrogenation) catalyst relative to the hydrocracking catalyst. If the amount of nitrogen in the feed is low, the catalyst ratio may be as low as 10:90 (by volume, denitrogenation:hydrocracking). In general, however, ratios between 25:75 to 75:25 will be used. With many stocks an approximately equal volume ratio will be suitable, for example 40:60, 50:50 or 60:40.

In addition to the denitrogenation function of the hydrotreating catalyst another and at least as important function is desulfurization since the sulfur content of the distillate product is one of the most important product specifications which have to be observed. The low sulfur products are more valuable and are often required by environmental regulation; the degree of desulfurization achieved is therefore of considerable significance. The degree of desulfurization obtained will be dependent in part upon the ratio of the hydrotreating catalyst to the hydrocracking catalyst and appropriate choice of the ratio will be an important factor in the selection of process conditions for a given feedstock and product specification. The degree of desulfurization will increase as the proportion of the hydrotreating catalyst increases and the lowest

sulfur contents consistent with the required conversion may be
obtained with an appropriate selection of the catalyst ratio.
Another function of the hydrotreating catalyst is to aid in the
saturation of polycyclic coke precurors and this, in turn, helps in
extending the life of the hydrocracking catalyst.

The degree of desulfurization is, of course, dependent upon
factors other than the choice of catalyst ratio. It has been found
that the sulfur content of the distillate product is dependent in
part upon the conversion and regulation of the conversion will
therefore enable the sulfur content of the distillate to be further
controlled: greater desulfurization is obtained at higher
conversions and therefore the lowest sulfur content distillates will
be obtained near the desired maximum conversion. Alternatively, it
may be possible to increase the degree of desulfurization at a given
conversion by raising the temperature of the hydrotreating bed while
holding the temperature of the hydrocracking bed constant. This may
be accomplished by appropriate use of hydrogen quenching.

The overall conversion may be maintained at a low level,
less than 50 volume percent to lower boiling products, usually
340°C- products from the heavy oil feedstocks used while still
maintaining satisfactory product quality. The conversion may, of
course, be maintained at even lower levels, for example 30 or 40
percent by volume. The degree of cracking to gas (C_4-) which
occurs at these low conversion figures is correspondingly low and so
is the conversion to naphtha (200°C-); the distillate selectivity of
the process is accordingly high and overcracking to lighter and less
desired products is minimized. It is believed that in cascade
operation this effect is procured, in part, by the effect of the
ammonia carried over from the first stage. Control of conversion
may be effected by conventional expedients such as control of
temperature, pressure, space velocity and other reaction parameters.

Surprisingly, it has been found that the presence of
nitrogen and sulfur compounds in the second stage feed does not
adversely affect catalyst aging in the absence of interstage
separation provided that sufficient denitrogenation catalyst is

employed.   Catalyst life before regeneration in this process may
typically be one year or even longer.   The extended operational life
of the hydrocracking catalyst in the presence of nitrogen and
sulfur, present as ammonia and hydrogen sulfide, respectively, in
the second stage feed is a surprising aspect of operation in the
cascade mode.   Further, the stability of the catalyst is even more
remarkable at the relatively low hydrogen partial pressures utilized
in low conversion operation.   Generally, the activity of cracking
catalysts is adversely and severely affected by nitrogen poisoning
and carbon (coke) deposition to such an extent that with an FCC
catalyst, for example, the coke deposition is so rapid that regene-
ration must be carried out continuously in order to maintain
sufficient activity.   In hydrocracking, the experience is that low
hydrogen partial pressures are conducive to more rapid coke
accummulation as the polycyclic coke precursors undergo polymeri-
zation; higher hydrogen pressure, on the other hand, tends to inhibit
coke formation by saturating these precursors before polymerization
takes place.   For these reasons, the excellent stability of the
hydrocracking catalyst in this process is quite unexpected.   The
zeolite beta hydrocracking catalysts are notable for their ability
to operate at relatively high conversions, for example at least 50%
conversion to 345°C- products under low hydrogen pressures;
conventional catalysts, by contrast, age rapidly under such
conditions.   When regeneration is, however, necessary, for example
after one year, it may be carried out oxidatively in a conventional
manner.

The conversion of the organic nitrogen compounds in the
feedstock over the hydrotreating catalyst to inorganic nitrogen (as
ammonia) enables the desire degree of conversion to be maintained
under relatively moderate and acceptable conditions, even with
relatively nitrogenous feedstocks.   Severe problems would be
encountered with nitrogenous feedstocks if the hydrotreating
catalyst were not used: in order to maintain the desired conversion
it would be necessary to raise the temperature but if the feedstock
is highly nitrogenous, it might be necessary to go to temperatures

at which the hydrocracking reactions become thermodynamically
unfavored. Furthermore, the volume of catalyst is fixed because of
the design of the plant and this imposes limits on the extent to
which the space velocity can be varied, thereby imposing additional
processing restrictions. The hydrotreating catalyst, on the other
hand, shifts the nitrogen content of the feedstock into inorganic
form in which it does not inhibit the activity of the catalyst as
much as it would if it were in its original organic form, even
though some reduction in activity is observed, as mentioned above.
Thus, higher conversion may be more readily achieved at reduced
temperatures, higher space velocities or both. Product distribution
will, however, remain essentially unaffected at constant conversion.

The present process has the advantage that it may be
operated in existing low pressure equipment. For example, if a
desulfurizer is available, it may be used with relatively few
modifications since the present process may be operated at low
pressures comparable to the low severity conditions used in
desulfurization. This may enable substantial savings in capital
costs to be made since existing refinery units may be adapted to
increase the pool of distillate products. If new units are to be
built there is still an economic advantage because the equipment
does not have to be designed for such high pressures as are commonly
used in conventional hydrocracking processes. However, minor
modifications may be necessary to existing equipment in order to
maintain operation within the nominal limits selected. For example,
a hydrodesulfurizer may require quench installation in order to keep
the temperature in the hydrocracking bed to the desired value;
alternatively, an additional reactor may be provided with appro-
priate quenching. The precise reactor configuration used will, of
course, depend upon individual requirements; the skilled person will
be able to appreciate and design the plant appropriately. An
exemplary hydrocracking unit without interstage separation is shown
in simplified form in U.S. Patent 4,435,275, to which reference may
be made for a description of it.

A particularly surprising attribute of the present process is that it is possible to use Pt/beta as the hydrocracking catalyst without interstage separation of heteroatoms. As is well known, platinum-containing catalysts are particularly prone to poisoning and it is therefore surprising that the Pt/beta functions as it does; in fact, compared to single stage hydrocracking without hydrotreating, less Pt/beta is required, other conditions being equal. Furthermore, the Pt/beta catalyst has been shown to be superior in hydroisomerization activity, as compared to NiW/beta, although its hydrocracking activity is lower than that of NiW/beta either in the cascade (no interstage separation) or two stage (interstage separation) modes. Because of this, the pour point obtained with the Pt/beta hydrocracking catalyst may be lower, for example by about 10°C than with the NiW/beta. The distillate selectivity of the Pt/beta catalyst may also be higher than that of the NiW/beta version under comparable conditions although the NiW/beta catalysts are also notable for giving higher rates of desulfurization and lower hydrogen consumption at equivalent conversions, depending upon the hydrotreating conditions. The Ni-W containing catalysts are also more active for conversion than the Pt-containing catalysts.

Compared to single stage hydrocracking, that is hydrocracking with a single catalyst, two-stage hydrotreating/hydrocracking (with interstage separation) achieves greater activity, permitting lower temperatures to be used, while using less zeolite, typically about 30 percent less. An improvement in distillate selectivity may also result. An additional benefit is that desulfurization and paraffin isomerization selectivity are also improved. Cascade processing without interstage separation provides product yields and qualities similar to those of separate two-stage processing without any major loss of conversion activity, although some loss of isomerization selectivity may ensue. However, any such loss may be compensated for by using a Pt/beta catalyst instead of a base metal catalyst, for example NiW/beta.

The hydrocracked products are low sulfur, low pour point distillates, generally containing less than 0.3 weight percent sulfur. Compared to the distillate products obtained by hydrocracking over conventional catalysts at low pressures (less than 7,000 kPa) using limited conversions, the product has a lower aromatic content. Zeolite beta hydrocracking catalysts gives a more paraffinic distillate product than conventional catalysts because it hydrocracks paraffins in preference to aromatics; conventional, amorphous hydrocracking catalysts by contrast, tend to act on the aromatics and at low pressures produce an even more aromatic product which is generally unsuitable for use as a jet fuel (aromatics conversion requires hydrogen for ring saturation and at low hydrogen pressures, the aromatics conversion will be limited, so that the product will be more aromatic). The products from zeolite beta are therefore highly satisfactory for use as jet and diesel fuels by reason of their highly paraffinic nature and low pour point; besides being relatively rich is iso-paraffins. The paraffinic character of the distillate also tends, to a certain extent, to dissolve any waxy paraffins which are present, so contributing further to good low temperature mobility characteristics. Thus, with the zeolite beta hydrocracking catalysts, aromatics are rejected in the bottoms (unconverted) fraction and a more highly paraffinic product is obtained, either in cascade or two-stage operation.

The process may be operated in different modes so as to alter the properties of the products. In particular, the process may be operated in a jet fuel mode to produce a highly paraffinic product with a notably low pour point; alternatively, it may be operated in a diesel fuel mode to produce an excellent diesel fuel with a high Diesel Index (Diesel Index is the product of the Aniline Point in degrees Fahrenheit ($°F = [°C.9/5] + 32$) and API Gravity/100), typically about 50-65, as compared to about 35 for known hydrocracking processes; although small quantities of gas and naphtha will be produced, the proportion of distillate range material will be enhanced relative to conventional processes operating at higher pressures and with higher conversions in multi-stage operations with interstage separation to remove ammonia.

The removal of sulfur in the higher boiling distillate oils is usually at least 90 percent complete so that these products will readily meet specifications for non-polluting fuel oils. The naphtha which is produced is characterized, like the other products, by a low heteroatom (sulfur and nitrogen) content and is an excellent feed for subsequent naphtha processing units, especially reforming units because of its high cycloparaffin content; the low heteroatom content enables it to be used in platinum reformers without difficulty. Because the zeolite beta hydrocracking catalysts can be operated at higher conversions under lower hydrogen pressures than conventional catalysts (without excessive aging) they are capable of achieving the desired conversion levels at lower severities than conventional catalysts (lower temperature, higher space velocity) and this means that the degree of desulfurization may be lower for a given conversion, resulting in a reduced hydrogen consumption, so that a smaller gas plant is required. The products can be made to meet applicable specification, for example 0.3 percent sulfur maximum, but the excessive desulfurization which accompanied high conversions with conventional zeolites under low pressures is avoided.

A particularly notable feature of the present process is that the bottoms product (345°C+) fraction is dewaxed during the hydrocracking so that it, too, has a lower pour point. Because of this, it has become possible to extend the distillate end point so as to increase the distillate pool yield. In the past, distillates such as jet fuel, diesel and heating oil have usually been held to a 345°C end point because the presence of waxy components in the higher boiling fractions precluded their inclusion in the distillate pool as pour point specifications would not have been met. With the present zeolite beta catalysts, however, the relatively low pour point of the higher boiling fraction permits some of it to be included in the distillate pool without exceeding pour point limitations. Generally, the distillate end point may be extended to about 400 or 415°C. Although, as mentioned above, the zeolite beta catalyst tends to reject aromatics to the high boiling fraction, the

presence of significantly higher amounts of paraffins in the 345°C-
(about 650°F-) fraction will reduce the final aromatics concentra-
tion in the product if an extended end point is taken. Either the
noble metal-containing catalysts, for example Pt/beta, or base metal
containing catalysts, for example NiW/beta, will permit a higher
product end point to be used for any given conversion than a
conventional amorphous catalyst which may be conversion limited
because of aging (aging is rapid with conventional catalysts at
conversions over about 40 percent but zeolite beta based catalysts
are capable of running at 70% conversion even at pressures below
7,000 kPa). Thus, the distillate pool is increased not only by the
better yield and the possibility of using higher conversions without
excessive catalyst aging but also by the prospect of raising the
distillate end point by a significant extent, all with a lower
hydrogen consumption and with improved product quality at any given
level of conversion.

As mentioned above, a number of improved product qualities
may be noted for the distillate fractions, including Pour Point (as
measured by ASTM D-97), Diesel Index and Smoke Point (ASTMD-1322).
These improvements are obtained, moreover, with reduced hydrogen
consumption and higher conversion and distillate yield. Although
the Aniline Points (ASTM D-611) of the products may be only slightly
higher than those obtained with conventional catalysts, their API
gravities are notably higher so that their Diesel Indices are
markedly higher. The distillate products are therefore highly
satisfactory diesel fuels.

The ability to improve the Diesel Index is notable since
conventional catalysts operating at low to moderate pressures below
7,000 kPa tend to give a relatively poor quality product, typically
of about 35 Diesel Index, as compared to a specification minimum of
53. Increasing the endpoint of the conventional product from about
345°C to a nominal 370°C would result in an improvement to about
DI=40. Further increases in end point would lead to additional
improvements in Diesel Index, typically to DI=42 but typical product
pour point specifications (-8°C) would preclude extension of the end

point in this manner. Upgrading of the product to the required specification would then require blending with straight-run kerosene. Use of the zeolite beta based catalyst would, by contrast, result in a distillate product of significantly improved quality even at conversions of 35 to 40%. For a full range distillate (165°-345°C) a Diesel Index of about 45 can be obtained and this can be increased to about 50 by raising the end point to a nominal 400°C, while the dewaxing function of the catalyst reduces the Cloud Point (ASTM D-2500) to about -7°C.. In addition, the pour point of the 400°C+ fraction is reduced to about 4°C. These improvements are attained, moreover, with no increases in net hydrogen consumption (about 80 n.l.l.$^{-1}$) relative to the process with the conventional catalyst. These improvements in product quality and operating economics may be attributed to the preferential conversion of paraffins over aromatics obtained with the zeolite beta catalysts.

The present process is particularly useful in the production of jet fuels which are characterized by a low Pour Point and good Smoke Points. This is particularly surprising given the low hydrogen pressures at which the process operates and which, with conventional catalysts, produces distillates of a pronounced aromatic character which cannot be used as jet fuels. The present jet fuels have an aromatic content below 40 volume percent, and usually below 30 volume percent, typically 20-30 volume percent. Smoke Points (ASTMD-1322) are usually in the range 15 to 30. Particularly surprising is that fuels of this kind are obtained at high conversions, for example over 40 or over 50 percent and at low specific hydrogen consumptions, for example not more than 100 or even 75 n.l.l.$^{-1}$.

This desirable result may be attributed to the aromatics rejection (to higher boiling fractions, specifically above 345°C), resulting from the use of zeolite beta.

The advantages of the present process may be perceived, moreover, not only in terms of product quality and yield and economy and stability of operation but also in overcoming certain limitations which may inhere in existing hydrocracking units. In general terms, these limits include:

1. Hydrogen consumption (the size of the gas plant-may preclude greater output),
2. Pressure limitation (equipment limits),
3. End Point limitation (limited by the Pour Point of the product which has to conform to specifications)
4. Limits on distillation capacity
5. Conversion limits (set by catalyst aging and hydrogen pressure)

Because the hydrogen consumption of the process is lower than that with the use of conventional catalysts, it may be possible to overcome the first limitation by using the present process - without a loss of product quality. Also, because the zeolite beta catalysts can operate at higher conversions under lower hydrogen pressures, e.g. below 10,000 kPa, even below 7,000 kPa, without excessive aging, limitations (2) and (5) can be circumvented. The End Point limitation can also be raised because, as mentioned above, the higher boiling fraction is effectively dewaxed as well as the distillate fraction. Thus, a number of the limitations inherent in the operation of existing hydrocracking units may be overcome by the use of the zeolite beta-containing catalysts.

The following Examples illustrate the invention.

Examples 1 & 2

These Examples compare single stage hydrocracking (Ex. 1) with two stage, separated hydrotreating/hydrocracking, that is with interstage separation (Ex. 2).

An Arab Light heavy vacuum gas oil (HVGO) (345°-580°C) was treated by the two processes, using NiW/beta catalysts (NiW/beta with Al_2O_3 binder, 50:50 zeolite:binder). The composition of the HVGO is given in Table 1 below. The conditions used and the results obtained are shown in Table 2 below.

Table 1
Arab Light HVGO I

API Gravity	22.2
Sulfur, wt. %	2.45
Pour Point, °C	40
KV, mm^2/s at 50°C	33.1

Table 2
HVGO Hydrocracking

	Ex. 1	Ex. 2
	Single-Stage[1] Once-Through	Two-Stage[2] Separated
Temperature, °C	428	385/412
Pressure, kPa	8720	8720/7000
LHSV	0.71	2.0/1.06 (0.67)
H_2 @ Inlet n.l.l.$^{-1}$	1394	712
(H) % wt.	(1.5)	(1.5)
H_2S+ NH_3	2.7	2.7
C_1-C_4	7.2	5.7
C_5-330°F Naphtha	18.5	15.8
165-345°C Distillate	37.0	37.7
345°C+	36.2	39.1
345°C+ Conversion, % wt.	63.8	60.9
H_2 Consumption n.l.l.$^{-1}$	151	149

Distillate Properties (3)

API Gravity	33.3	33.7
Diesel Index	37	41
Pour Point, °C	-54	-45
KV mm^2/s @ 50°C	1.8	1.9

	Ex. 1	Ex. 2
	Single-Stage[1] Once-Through	Two-Stage[2] Separated
345°C+ Properties		
API Gravity	-	-
Sulfur % wt.	0.03	0.02
Pour Point, °C	-1	-1
KV mm^2/s @ 50°C	-	24.5
% Zeolite used	50	33

Notes:

1. NiW-Mg Beta/Al$_2$O$_3$ (50/50)

2. NiMo/Al$_2$O$_3$ (Harshaw HDN-30); NiW-HBeta/Al$_2$O$_3$ (50/50 steamed 24 hours HNa$^+$)

3. Distillate is 165-345°C

Examples 3 - 5

Hydrocracking was carried out using the same HVGO feed as in Examples 1 and 2, but with a Pt/beta catalyst. The operation modes were single stage (Ex. 3), and two stage, separated (Ex. 4). For comparison, a cascade operation (no interstage separation) is shown in Example 5, using a slightly different feed containing about 5 percent 345°C- products, but with the results normalized to a 345°C+ basis. The conditions used and results obtained are shown in Table 3 below.

Table 3
Pt/Beta Hydrocracking

	Ex. 3 Single-Stage	Ex. 4 Two-Stage Separated	Ex. 5 Two-Stage(1) Cascade
Temperature, °C	414	385/413	415
Pressure, kPa	7000	8720/7000	5962
LHSV	0.67	2.0/1.0 [0.67]	0.5
H_2 @ Inlet n.l.l.$^{-1}$	712	712	534
(H) % wt.	(0.2)	(1.4)	(0.7)
H_2S+ NH_3	0.6	2.6	2.5
C_1–C_4	0.8	1.0	1.4
C_5–165°C Naphtha	4.1	5.9	7.6
165–345°C Distillate	23.0	33.4	33.1
345°C+	71.6	58.0	55.9
345°C+ Conversion, % wt.	28.4	42.0	44.1
H_2 Consumption n.l.l.$^{-1}$	19.6	144	765
Distillate Properties			
API Gravity	–	34.5	34
Diesel Index	–	47.1	45
Pour Point, °C	–	-29	-34
KV mm^2/s @ 50°C	–	1.8	1.8
345°C+ Properties			
API Gravity	–	–	28.6
Sulfur % wt.	1.34	0.08	0.03
Pour Point, °C	21	-4	4
KV mm^2/s @ 50°C	–	27.1	16.5
% Zeolite used	50	33	25

Notes:
1. VGO Feed – data normalized on 345°C+ basis

Example 6

An Arab Light HVGO having the properties shown in Table 4 below was evaluated in a cascade mode hydrotreating/hydrocracking process using a commercial Ni-Mo/Al$_2$O$_3$ hydrotreating catalyst in the first stage. A number of different catalysts were used in the second half of the reactor, including Pt/beta, NiW/beta and two conventional, commercially available hydrocracking catalysts (identified as A and B). The process conditions used were 5960 kPa, 0.50 LHSV and 535 n.l.l^{-1} H$_2$ (inlet) with the reactor temperature adjusted between 400 and 430°C to obtain various conversions.

Table 4
Arab Light HVGO II

API Gravity	23.2
Sulfur, wt. %	2.3
Nitrogen, ppm	550
Pour Point, °C	35
345°C-, wt. %	7

The results are shown in Figure 1 which relates the pour point of the 345°C+ fraction to the conversion attained, using the different hydrocracking catalysts. For comparison, the Figure also shows the results obtained using interstage separation.

The figure shows that the hydrocracking catalysts containing zeolite beta as the acidic component dewax unconverted gas oil. The Pt/beta catalyst has a greater selectivity for paraffin isomerization resulting in low pour point products at moderate boiling range conversions. Hydrogen consumption with the Pt/beta catalyst at 50% conversion was about 85 n.l.l.$^{-1}$.

Example 7

The Arab Light HVGO II of Table 4 was subjected to cascade hydrotreating – hydrocracking (no interstage separation) using a conventional hydrotreating catalyst and a Pt/beta hydrocracking catalyst (0.6% Pt). The process was operated at about 5960 kPa pressure, with conditions (temperature, space velocity) adjusted to give 46.5 weight percent 345°C+ conversion. The product qualities are set out below in Table 5.

Table 5
Product Quality

Nominal Boiling Range °C 93% TLP	I-120	120-165	165-195	195-260	260-345	345-400	400+
As Cut Yield % Wt.	1.5	4.5	4.6	9.0	23.1	22.1	28.2
API	-	-	44.1	37.2	31.5	29.8	27.8
SG 15°C	-	-	0.8060	0.8390	0.8683	0.8771	0.8885
Hydrogen % Wt.	(14.45)	(13.82)	-	-	-	-	-
Sulfur	-	-	-	-	-	-	-
Nitrogen ppmw	-	-	-	-	0.012	0.030	0.024
CCR	-	-	-	-	-	-	-
Paraffins % Wt.	52.9	46.2	41.3		33.6	41.2	29.9
Naphthenes, % Wt.	32.9	29.7	28.5		22.9	18.8	33.6
Aromatics, % Wt.	14.2	24.1	30.2		43.5	40.0	36.5
Aniline Point °C				48	62	79	95
Cloud Point °C				-41	-9	4	-
Pour Point °C	-	-	-	HZY	-20	2	7
Smoke Point mm.	-	(21.5)	(16.3)	(12.0)	-	-	-
KV mm^2/s @ 40°C	-	-	-	1.165	4.343	11.29	41.04
KV mm^2/s @ 100°C	-	-	-	-	-	2.781	6.290
Diesel Index	-	-	-	43.8	44.8	51.9	56.5

Example 8

A hydrocracking operation was carried out using a NiW/beta
hydrocracking catalyst (4% Ni, 10% W, zeolite: alumina 50:50;
steamed 24 hours in H-Na form 540°C, 90% steam in air, atmospheric
pressure). The feed was the Arab Light HVGO II of Table 4. The
stability of the operation together with selected product properties
can be seen from Table 6 below.

Table 6
Niw/Beta Hydrocracking

Days on Stream	61.6	68.6	71.8	73.6	78.8	84.3
Temp. °C	399	413	413	413	417	408
Press. kPa	5960	5960	5960	5960	5960	5960
LHSV	0.47	0.49	0.49	0.48	0.48	0.48
H2 n.l.l.-1 inlet	535	535	535	535	535	535
345°C+ Conversion % wt	28.6	64.7	57.6	57.6	73.7	41.9
H2 Consumption n.l.l.-1	56	95	80	76	103	71
(H) % wt	(0.52)	(0.88)	(0.74)	(0.70)	(0.95)	(0.66)
H2S + NH3	2.28	2.45	2.44	2.44	2.45	2.37
C1 - C4 % wt	0.83	5.48	3.18	3.16	7.05	1.93
C5 - 165°C Naphtha	4.28	20.80	15.99	15.97	25.00	8.07
165-345°C Distillate	26.72	39.33	39.68	39.68	41.98	34.28
345°C+	66.41	32.79	39.46	39.46	24.46	54.00
Distillate as cut % wt	21.3%	34.8%		38.6%	39.7%	(25.2%)
API	33.4	33.7		34.8	34.6	34.8
SG, 15°C	0.858	0.8568		0.8510	0.8520	0.8508
Hydrogen, % wt.	12.46	12.63		12.89	12.75	12.82
Sulfur, % wt.	-	0.004		0.012	0.010	0.012
Aniline Point, °C	50	53		52	50	50
Diesel Index	40.7	42.8		43.9	42.0	42.5
Pour Point °C	-26	-32		-54*	-37	-37
KV mm2/s @ 40°C	2.762	2.549		2.333	2.197	2.190
Bottoms as cut % wt	72.2	38.0		41.1	29.0	(63.8%)
SG, 15°C	0.8944	0.8944		0.8922	0.9072	-
Hydrogen, % wt.	13.14	12.72		12.76	12.32	12.97
Sulfur, % wt.	(0.12)	0.072		0.086	0.100	0.135
Nitrogen, ppmw	(240)	120		120	120	170
P/N/A**	30/32/38	29/30/41		29/30/41	24/30/46?	28/32/40
Pour Point °C	45	2		7	-7	15
KV mm2/s @ 40°C	25.62	20.93		22.57	22.62	21.99
KV mm2/s @ 100°C	4.731	3.996		4.230	4.072	4.284

* Less than
** Paraffins/Naphthenes/Aromatics, % wt.

Example 9

Using the same feed and process conditions as in Example 8,
the hydrocracking operation was repeated, but using a Pt/beta
hydrocracking catalyst (0.6% Pt; zeolite:alumina 50:50; steamed 72
hours in H-Na form, 540°C, 90% steam in air, atmospheric pressure).
The results are shown in Table 7 below.

Table 7
Pt/Beta Hydrocracking

Days on Stream (avg)	57	60	64	75	81
Temperature °C	417/412	417/412	417/412	422/423	422/424
Pressure kPa (psig)	5960 (850)	5960 (850)	5960 (850)	5960 (850)	5960 (850)
345°C+ Conversion % Wt	52.4	46.5	44.1	69.2	65.9
H$_2$ Consumption n.l.l.$^{-1}$	114	83	74	116	124
(H)	(1.05)	(0.76)	(0.56)	(1.06)	(1.14)
H$_2$S + NH$_3$	2.47	2.44	2.43	2.45	2.43
C$_1$ – C$_4$ % wt	3.05	2.19	1.30	4.39	4.84
C$_5$ – 165°C Naphtha	10.48	8.70	7.06	18.45	17.55
165 –345°C Distillate	40.77	37.67	37.81	47.08	44.54
345°C+	44.32	49.76	51.97	28.69	31.76
165/345/400°C					
Distillate as cut % wt	54.5%	36.7%	35.4%	42.7%	49.1%
API	33.8	34.4	34.5	36.8	34.5
SG @ 15°C	0.8560	0.8528	0.8533	0.8437	0.8567
Hydrogen, % wt.	13.13	13.01	12.98	13.08	12.88
Sulfur, % wt.	0.002	0.008	0.004	0.006	0.012
Aniline Point °C	68	57	56	58	60
Diesel Index	52.2	46.1	45.5	50	48.3
Pour Point °C	-20	-43	-29	-54*	-40
KV mm^2/s @ 40°C	4.38	2.654	2.666	2.294	3.32
Bottoms as cut % wt	27.2%	50.3	53.7%	30.4%	23.0%
345/400°C API	28.2	28.7	28.6	25.3	24.1
SG @ 15°C	0.8935	0.8835	0.8840	0.9024	0.9096
Hydrogen, % wt.	13.09	12.95	13.06	12.43	12.37
Sulfur, % wt.	0.008	0.026	0.026	0.026	0.032
Nitrogen, ppmw	184	170	160	170	200
P/N/A**	32/33/35	31/31/38	32/30/38	28/27/45	23/33/44
Pour Point °C	2	7	4	-32	-32
KV mm^2/s @ 40°C	36.51	22.27	21.81	19.53	37.56
KV mm^2/s @ 100°C	5.749	4.299	4.24	3.75	5.56
Aniline Pt, °C		89			

* Less than ** Paraffins/Naphthenes/Aromatics, % wt.

CLAIMS:

1. A hydrocracking process for making a highly paraffinic, low pour point distillate product from a heavy hydrocarbon oil feed boiling substantially above 345°C, which comprises:

    (i) passing the heavy oil feed over a hydrotreating catalyst in the presence of hydrogen at elevated temperature and at a hydrogen partial pressure of not more than 10,000 kPa to hydrotreat the oil;

    (ii) passing the hydrotreated oil from step (i) over a hydrocracking catalyst comprising zeolite beta and a hydrogenation-dehydrogenation component in the presence of hydrogen at elevated temperature and at a hydrogen partial pressure of not more than 10,000 kPa to hydrocrack the oil at a bulk conversion of at least 40 weight percent and;

    (iii) recovering from the hydrocracked product from step (ii) a fraction boiling below 345°C.

2. A process according to Claim 1, in which the hydrotreating and hydrocracking steps are carried out at pressures below 7,000 kPa.

3. A process according to Claim 1 or Claim 2, in which the conversion is at least 50 weight percent.

4. A process according to any one of Claims 1 to 3, in which the 345°C-fraction has a pour point not higher than -20°C.

5. A process according to any one of Claims 1 to 4, in which the 345°C+ product has an aromatics' content of at least 40 percent.

6. A process according to Claim 5, in which the 345°C-fraction has a sulfur content from 0.01 to 0.3 weight percent.

7.   A process according to Claim 5 or Claim 6, wherein the 345°C- fraction includes a fraction boiling above 165°C having a Diesel Index of at least 40.

8.   A process according to Claim 7, in which the fraction boiling above 165°C has a Pour Point (ASTM D-97) not higher than -20°C.
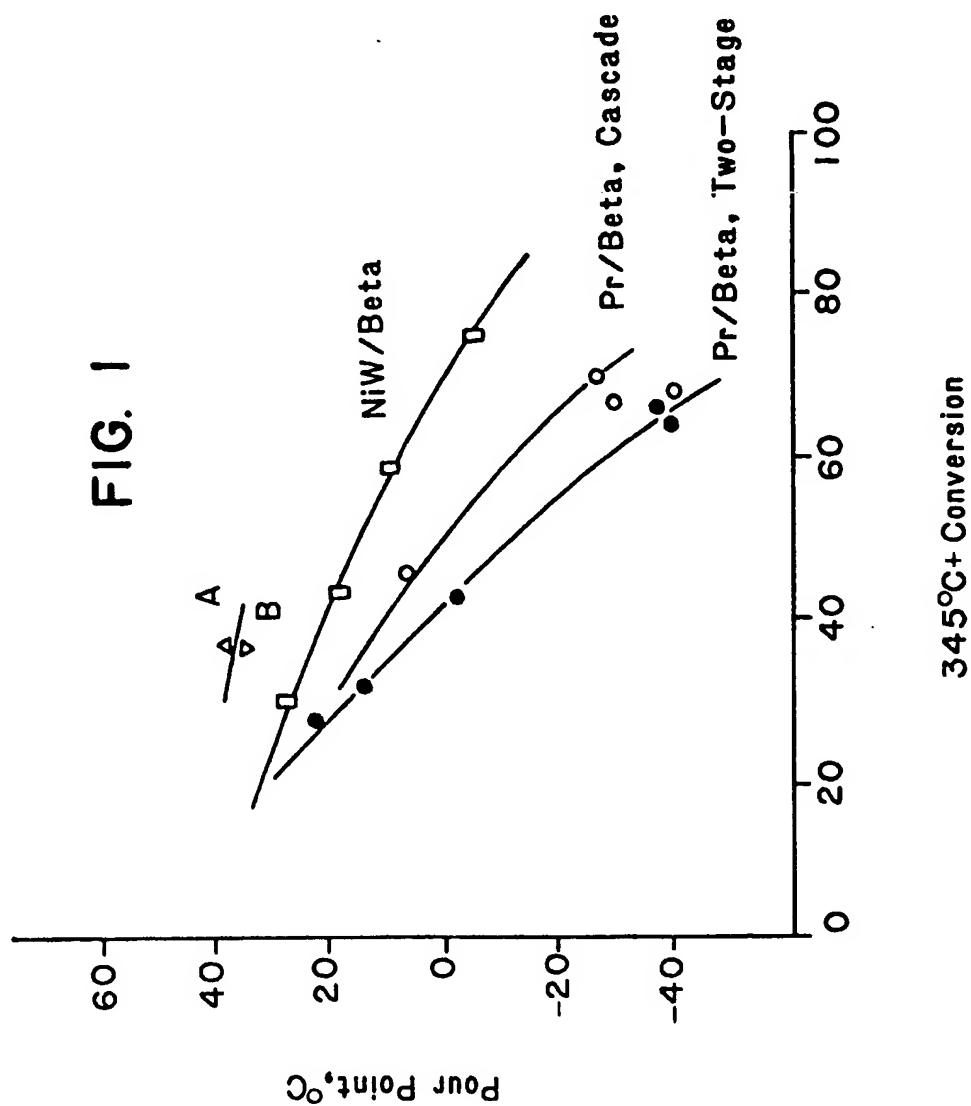
9.   A process according to any one of Claims 1 to 4, in which the 345°C- fraction is a jet fuel having an aromatics' content below 40 volume % and a paraffin content above 30 volume %.

10.   A process according to Claim 9, in which the jet fuel has an aromatics' content below 30 volume % and a paraffin content above 40 volume %.

11.   A process according to Claim 9 or Claim 10, in which the jet fuel has a Smoke Point of 15 to 30.

12.   A process according to any one of Claims 9 to 11, in which the hydrogen consumption is not more than 100 n.l.l.^{-1}.

13.   A process according to any one of Claims 9 to 12, in which the jet fuel has a Pour Point not higher than -40°C.

FIG. 1

European Patent Office

EUROPEAN SEARCH REPORT

	DOCUMENTS CONSIDERED TO BE RELEVANT		EP 86304601.7

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP - A1 - 0 094 827 (MOBIL OIL CORPORATION) * Claims; abstract * --	1	C 10 G 49/08 C 10 G 45/64
A	GB - A - 1 311 431 (ATLANTIC RICHFIELD COMPANY) * Claims; page 1, lines 46 - page 3, line 42 * --	1	
A	GB - A - 1 263 289 (ESSO RESERCH AND ENGINEERING COMPANY) * Claims; page 1, line 31 - page 4, line 89 * ----	1	

			TECHNICAL FIELDS SEARCHED (Int Cl 4)
			C 10 G 49/00 C 10 G 45/00 C 10 G 47/00 B 01 J 29/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	25-11-1986	STÖCKLMAYER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03 03